Egypt. J. Rad. Sci. Applic. **Vol. 33,** No.2, pp. 101-105 (2020)

Egyptian Journal of Radiation Sciences and Applications
http://ejrsa.journals.ekb.eg/

EGYPTIAN ATOMIC ENERGY AUTHORITY

Fast Procedure for Aqueous Samples Investigation Using SEM and EDX for Nuclear Safeguards Purposes

S.E. Shaban[#], K.A. El-adham, W.F. Khalil
Egyptian Nuclear and Radiological Regulatory Authority (ENRRA), P.O. Box 7551, Cairo, Egypt.

SAFEGUARDS technical measures applied on nuclear materials and activities aim at detecting and determining whether the samples are nuclear or not. For this purpose, SEM and EDX are used for fast detection of uranium and thorium within samples, but these tools stand helplessly in the case of liquid samples. Such samples need tools and further preparation to be appropriate for measurements. Graphene oxide (GO) is employed as an adsorbent for uranium because it contains various functional groups such as epoxide, carbonyl, carboxyl and hydroxyl in addition to its high specific surface area. The product of the adsorption process is measured using SEM and EDX. The as-prepared GO has been prepared then characterized using SEM, TEM, and XRD then undergone adsorption with different concentrations of uranium. The results showed that the prepared materials are efficient adsorbents for the removal of uranium from water and hence can be used to detect and determine uranium in samples.

Keywords: EDX, Graphene oxide, SEM, Uranium.

Introduction

Nuclear safeguards is a system of technical measures employed to make sure that fissionable materials are utilized for their intended purposes and are under control by implementing technologies, policies, and procedures (IAEA, 2014).

Accounting and controlling nuclear materials is the backbone for safeguards implementation and it is also an important factor for successful security undertakings. It manages the process of registering sensitive materials by accurately maintaining bookkeeping and following changes in material inventory (IAEA, 2008). Continuous measuring of nuclear material and facility operating data are employed to get up-to-date information. The accounting system is not only responsible for maintaining the bookkeeping of nuclear inventory, but also responsible for tracking their locations and movements (Gavron, 2001).

The records and reports done by the accounting system are subject to auditing by the national and international inspection authorities through verification and measurement of nuclear materials to confirm correctness and completeness (Goldman, 1994).

A scanning electron microscope (SEM) uses incident electrons over a surface to get an image. The electron beam interacts with the sample and produces different signals that can be utilized to get topography and composition information (Jeol co. website).

SEM creates images by scanning the sample with a high-energy beam of electrons. Once interaction occurs between electrons and the substance, secondary electrons, backscattered electrons, and characteristic X-rays are produced (Reed, 1975). These signals are detected to get images that are displayed on a screen. When the incident beam hits the sample surface, it penetrates a few microns in the surface based on the voltage and the sample density. Many signals,

[#]Corresponding author email: smh_elsaid@yahoo.com
Received 28/11/2020; Accepted 23/12/2020
DOI: 10.21608/ejrsa.2020.51426.1108

such as reflected electrons, secondary electrons and X-rays, are emitted because of this interaction within the sample.

Energy-dispersive X-ray spectroscopy (EDX) is an analytical technique where a beam of electrons hits the specimen, resulting in the excitation of an inner shell electron, causing its emission and the formation of a hole. This technique is valid for fast qualitative and semi-quantitative analyses.

Graphite oxide is a compound that consists of variable ratios of carbon, oxygen, and hydrogen, obtained by treating graphite with strong oxidizers. The maximally oxidized bulk product is a yellow solid with C:O ratio between 2.1 and 2.9, that retains the layer structure of graphite, but with much larger and irregular spacing. The bulk material spontaneously disperses in basic solutions or can be dispersed by sonication in polar solvents to yield monomolecular sheets, known as graphene oxide by analogy to graphene, the single-layer form of graphite (Marcano et al., 2010). Graphene oxide sheets have been used to prepare strong paper-like materials, membranes, thin films, and composite materials. Initially, graphene oxide attracted substantial interest as a possible intermediate for the manufacture of graphene. The graphene obtained by reduction of graphene oxide still has many chemical and structural defects which are considered a problem for some applications, but an advantage for some others (El Rouby et al., 2018).

Li et al., developed a thin sheet of GO by the hummer method and used it for the adsorption of U (VI) ions. They reported a value of 299 mg/g for the adsorption capacity (Li, 2012).

Guixia Zhao et al., utilized nano sheets of GO to act as adsorbents for U(VI) ions. They achieved U(VI) sorption of 97.5 mg/g (Zhao, 2011).

Experimental

Materials

The following materials have been used as received without further purification: graphite fine powder extra pure (particles size < 50 µm from Merck Company) has been used for GO synthesis. Other reagents, sulphuric acid (98% H_2SO_4), phosphoric acid (95% H_3PO_4), hydrochloric acid (36.5% HCl), absolute ethanol were purchased from Sigma-Aldrich. Potassium permanganate ($KMnO_4$), Sodium hydroxide (NaOH) and hydrogen peroxide (30% H_2O_2) were supplied by Alfa Company, India.

Graphene oxide preparation

GO was prepared from graphite powder using the improved Hummers' method with slight modification. Briefly, under vigorous stirring in ice path concentrated H_2SO_4 (90 ml) and H_3PO_4 (60 ml) was added slowly to $KMnO_4$ (20 g). Second, the obtained past was added to 30 ml H_2O_2(30 wt %), the color of the mixture changed from brown to yellow. Then, it was exfoliated in water by ultra-sonic waves for 2 h at room temperature. Third, GO was washed by HCl (5%) and deionized water several times by centrifuge (10,000 rpm for 30 min.) until pH reached ~ 6. Finally, the resultant GO was dried under a vacuum oven at 60 °C overnight.

Characterization of GO

Shimadzu XRD-6000 X-ray diffractometer was used to get the XRD results of GO. The measurements were carried out at anode current values of 40 Kv and 30 mA. The range of scan extended from 5° to 90° with a speed of 8 (deg/min) and preset time 0.15 sec.

JEOL Model 2100, high-resolution transmission electron microscopy (HRTEM) was used to study the morphology of GO. The sample was prepared by making a suspension of a certain amount of powder in a tube filled with distilled water. To avoid or reduce particle agglomeration, sonication was done for half an hour. An appropriate amount of the suspension was placed on a carbon grid and dried to be valid for use in TEM.

The X-ray diffraction (XRD) patterns of GO composites were recorded using X-ray diffractometer, PANalytical Empyrean with Cu radiation λ=1.54056 Å. The 2θ scan ranging from 5˚ to 90˚ continuous scanning with scan speed 8 (deg/min) was used for the entire 2θ-range.

Adsorption of uranium on graphene oxide

Uranium solutions with different concentrations ranging from 0.1% to 0.6% were used in the adsorption process with graphene oxide and the resulted adsorbent was dried to be suitable for imaging and analysis using SEM and EDX.

Results and Discussion

Characterization of GO

Go is characterized using various tools. Figures 1-3 demonstrate the results of XRD, TEM and Raman spectroscopy for the prepared GO.

The XRD diffraction patterns of GO is shown in Fig. 1. A sharp peak appeared at 2 θ = 10.2° which is characteristic to (002) diffraction plan of pure GO.

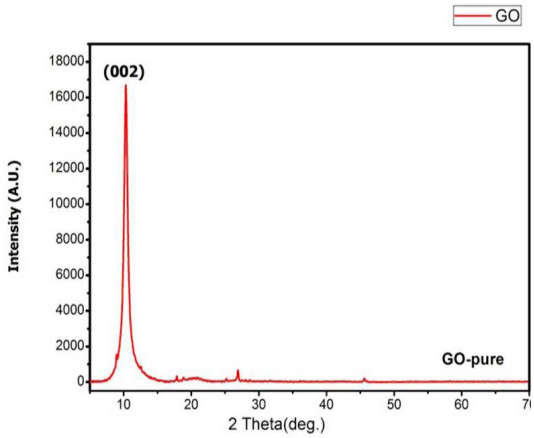

Fig. 1. XRD spectrum of GO

Figure 2 shows HRTEM image of the prepared GO. The HRTEM image of GO prepared by improved Hummers method shows the layered structure of 2D graphene oxide appeared flat and transparent, with some wrinkles and folding on the surface.

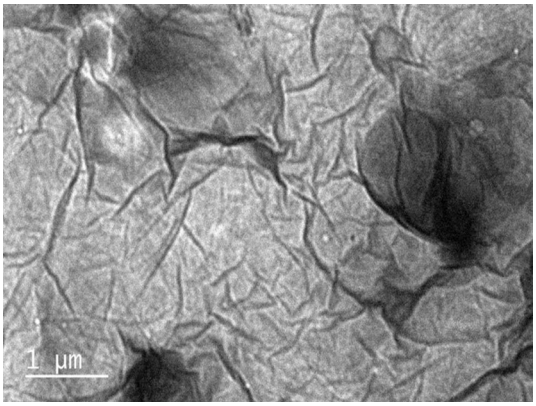

Fig. 2. HRTEM image of graphene oxide

Raman spectroscopy is a very useful tool for characterizing GO. The spectra results of Raman spectroscopy are shown in Fig. 3. The recorded Raman spectroscopy of GO shows the appearance of two major bands; D-band at 1358 cm^{-1} and G-band at 1596 cm^{-1}. The D and G band intensity ratio (ID/IG) equal to 0.9945.

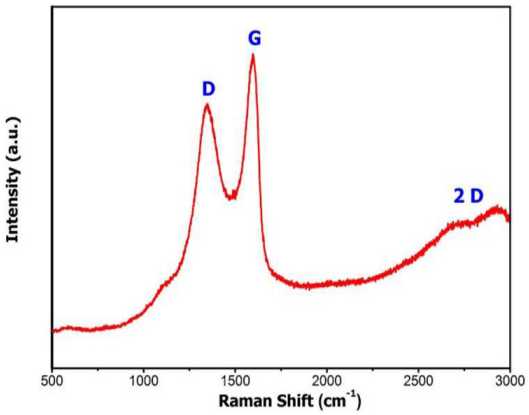

Fig. 3. Raman spectrum of GO

Adsorption of uranium on GO

Uranium is adsorbed on GO and the result of adsorption is mounted on a filter paper after undergoing drying to analyze it. Figures 4–9 demonstrate the SEI image of different concentrated uranium samples scanned with SEM at ideal conditions of evacuation and working distance.

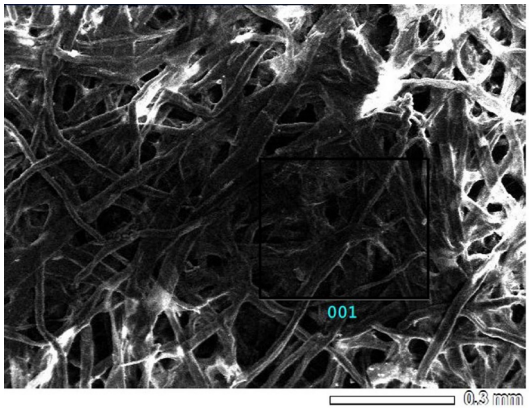

Fig. 4. SEM image of STU1 sample

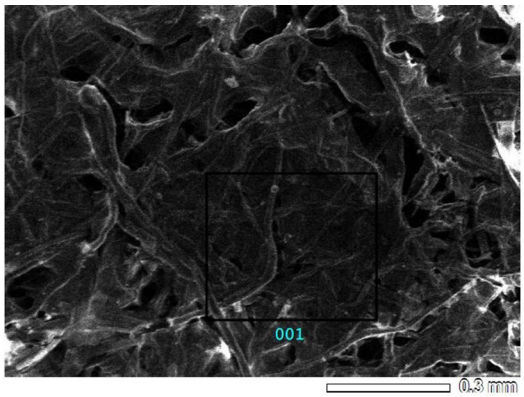

Fig. 5. SEM image of STU2 sample

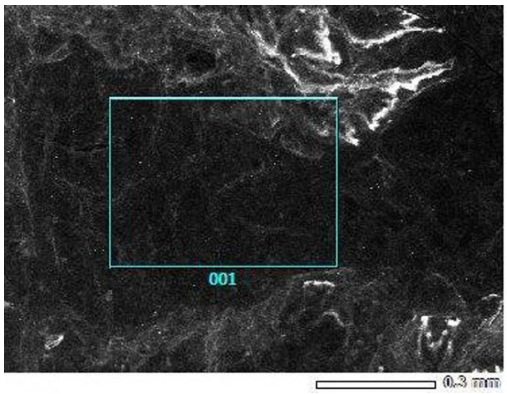

Fig. 6. SEM image of STU3 sample

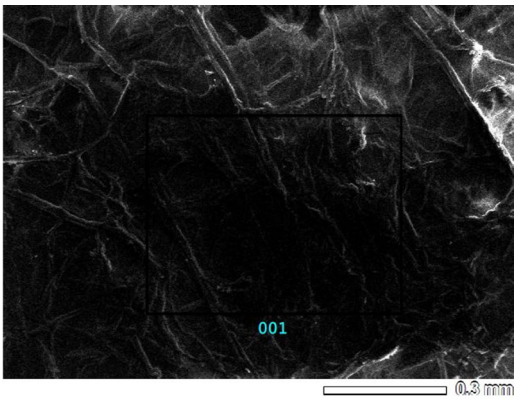

Fig. 7. SEM image of STU4 sample

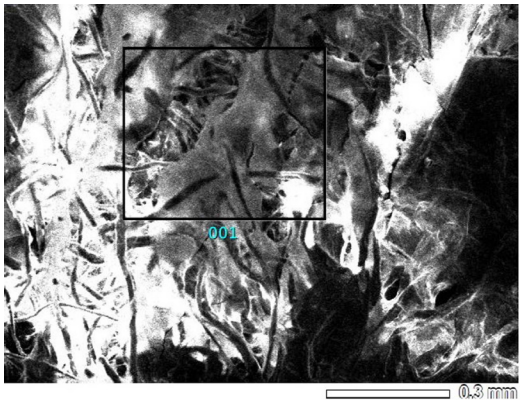

Fig. 8. SEM image of STU5 sample

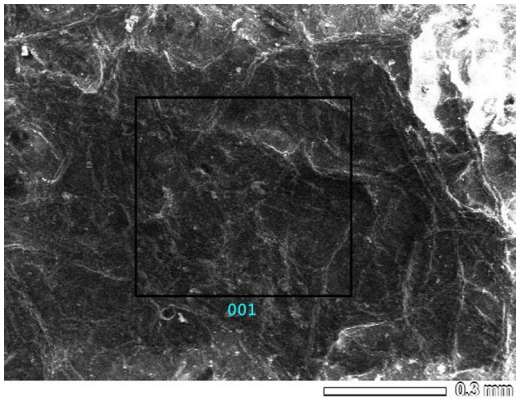

Fig. 9. SEM image of STU6 sample

After scanning the samples, they were analyzed using an EDX instrument attached with SEM. The resulted EDX spectrum demonstrates the peaks for an element within the samples. The peak of interest for the safeguard inspector is the uranium peak. Figure 10 demonstrates the EDX spectrum for one of the samples in which the uranium peak appeared at a characteristic x-ray value equal to 3.164 keV.

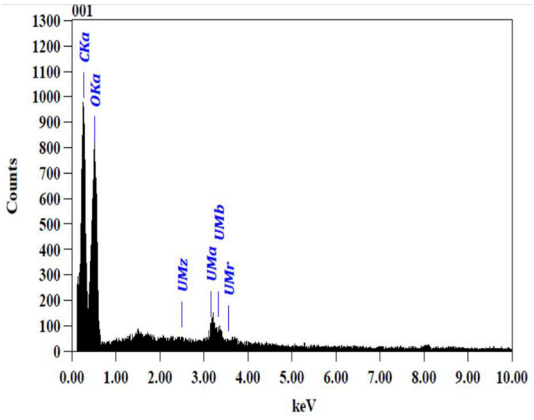

Fig. 10. EDX spectrum of the adsorption process

All samples were analyzed and the uranium mass percentage in each sample was registered with the corresponding relative uncertainty. Table 1 demonstrates that the uranium mass percentage increases as the concentration of the adsorbed uranium increases.

TABLE 1. Concentration of uranium (mass%) in all samples

Sample code	Uranium mass (Mass % ± σ_M %)
STU1	7.00 ±1.09%
STU2	11.810.93%±
STU3	15.871.00%±
STU4	19.130.98%±
STU5	22.710.99%±
STU6	26.480.94%±

Conclusion

Graphene oxide was prepared by the improved Hammer method. Tools such as TEM, XRD and Raman spectroscopy were used to characterize the prepared GO. GO was successfully applied as an adsorbent for removal of uranium from

aqueous solutions and the resultant was subjected to analysis by SEM and EDX. This method was used to image uranium particles adsorbed on the surface of the graphene oxide by SEM then EDX to analyze the selected particle or area. The method overcomes the problem of screening samples containing uranium in the liquid phase. This method proved to be effective to detect uranium for safeguards purposes.

Disclosure Statement: No potential conflict of interest was reported by the authors.

References

El Rouby, W.M., Farghali, A.A., Sadek, M.A., Khalil, W.F. (2018) Fast removal of Sr (II) from water by graphene oxide and chitosan modified graphene oxide. *Journal of Inorganic and Organometallic Polymers and Materials*, **28**(6), 2336-49.

Gavron, A. (2001) Non destructive assay techniques applied to nuclear materials. *9th International Conference on Nuclear Engineering*, France.

Goldman. I.N. (1994) Environmental sampling and analysis. IAEA-SM-33\97, *International Nuclear Safeguards Proceedings*,Vol. 1.

IAEA. (2008) Nuclear Material Accounting. services series 15.

IAEA. (2014) Guidance for States Implementing Comprehensive Safeguards Agreements and Additional Protocols. service series 21 (updated).

Li, Z., Chen, F., Yuan, L., Liu, Y., Zhao, Y., Chai, Z., Shi, W. (2012) Uranium (VI) adsorption on graphene oxide nanosheets from aqueous solutions. *Chemical Engineering Journal*, **210**, 539-546.

Marcano, D.C., Kosynkin, D.V., Berlin, J.M., Sinitskii, A., Sun, Z., Slesarev, A., Alemany, L.B., Lu, W., Tour, J.M. (2010) Improved synthesis of graphene oxide. *ACS Nano*, **4**(8), 4806-14.

Reed, S.J.B. (1975) "*Electron Microprobe Analysis*" London, New York, and Melbourne, Cambridge University Press, 399p.

Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) manual, JeolURL: http://www.Jeol.com/products/electronoptics/scanningelectronmicroscopessem/analyticalsem/jsm6510a6510la/tabid/602/default.aspx

Zhao, G., Li, J., Ren, X., Chen, C., Wang, X. (2011) Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management. *Environmental Science & Technology*, **45**(24), 10454-10462.